

GLOSSARY OF TERMS USED IN PHYSICAL ORGANIC CHEMISTRY (IUPAC Recommendations 1994)

I

Continued from terms starting with H

Contents

identity reaction; imbalance; + imene; + imidogen; + imidonium ion; + imin; + imine radical; inclusion compound (or inclusion complex); induction period; inductive effect; inductomeric effect; inert; inhibition; initiation; inner-sphere (electron transfer); insertion; intermediate; intermolecular; internal return; intimate ion pair; intramolecular; intramolecular catalysis; intrinsic barrier; inverse kinetic isotope effect; inverted micelle; ionic strength; ionization; ionization energy; ionizing power; ion pair; ion pair return; ipso-attack; isodesmic reaction; isoelectronic; isoentropic; isoequilibrium relationship; isokinetic relationship; isolobal; isomer; isomerization; isosbestic point; isoselective relationship; isotope effect; isotope effect, equilibrium; isotope effect, heavy atom; isotope effect, intramolecular; isotope effect, inverse; isotope effect, kinetic; isotope effect, primary; isotope effect, secondary; isotope effect, solvent; isotope effect, steric; isotope effect, thermodynamic; isotope exchange; isotopic perturbation, method of; isotopic scrambling; isotopologue; isotopomer; isovalent hyperconjugation

identity reaction

A *chemical reaction* whose products are chemically identical with the reactants, for example the bimolecular self exchange reaction of CH_3I with I^- . See also *degenerate rearrangement*.

imbalance

The situation in which *reaction* parameters that characterize different bond forming or bond breaking processes in the same reaction have developed to different extents as the *transition state* is approached along some arbitrarily defined reaction coordinate. For example, in the nitroalkane anomaly, the Brønsted β exponent for proton removal is smaller than the Brønsted α for the nitroalkane, because of imbalance between the amount of bond breaking and resonance delocalization in the transition state. Imbalance is common in reactions such as elimination, addition and other complex reactions that involve proton (hydron) transfer. BERNASCONI (1992). See also *synchronous*, *synchronization (principle of imperfect synchronization)*.

+ imene

See *nitrene*.

+ imidogen

See *nitrene*.

+ imidonium ion

See *nitrenium ion*.

+ imin

See nitrene.

+ imine radical

See nitrene.

inclusion compound (or inclusion complex)

A complex in which one component (the host) forms a cavity or, in the case of a crystal, a crystal lattice containing spaces in the shape of long tunnels or channels in which molecular entities of a second chemical species (the guest) are located. There is no covalent bonding between guest and host, the attraction being generally due to van der Waals forces. If the spaces in the host lattice are enclosed on all sides so that the guest species is "trapped" as in a cage, such compounds are known as "clathrates" or "cage" compounds".

induction period

The initial slow phase of a chemical reaction which later accelerates. Induction periods are often observed with radical reactions, but they may also occur in other systems (for example before steady-state concentration of the reactants is reached).

inductive effect

In strict definition, an experimentally observable effect (on rates of reaction, etc.) of the transmission of charge through a chain of atoms by electrostatic induction. A theoretical distinction may be made between the field effect, and the inductive effect as models for the Coulomb interaction between a given site within a molecular entity and a remote unipole or dipole within the same entity. The experimental distinction between the two effects has proved difficult, except for molecules of peculiar geometry, which may exhibit "reversed field effects". Ordinarily the inductive effect and the field effect are influenced in the same direction by structural changes in the molecule and the distinction between them is not clear. This situation has led many authors to include the field effect in the term "inductive effect". Thus the separation of σ values into inductive and resonance components does not imply the exclusive operation of a through-bonds route for the transmission of the non-conjugative part of the substituent effect. To indicate the all-inclusive use of the term inductive, the phrase "so-called inductive effect" is sometimes used. Certain modern theoretical approaches suggest that the "so-called inductive effect" reflects a field effect rather than through-bonds transmission. EHRENSON, BROWNLEE and TAFT (1973); TAFT and TOPSOM (1987). See also field effect, mesomeric effect, polar effect.

inductomeric effect

A molecular polarizability effect occurring by the inductive mechanism of electron displacement. The consideration of such an effect and the descriptive term have been regarded as obsolescent or even obsolete, but in recent years theoretical approaches have reintroduced substituent polarizability as a factor governing reactivity, etc. and its parametrization has been proposed. See TAFT and TOPSOM (1987); INGOLD (1953).

inert

Stable and unreactive under specified conditions.

inhibition

The decrease in rate of reaction brought about by the addition of a substance (inhibitor), by virtue of its effect on the concentration of a reactant, catalyst or reaction intermediate. For example, molecular oxygen and *p*-benzoquinone can react as "inhibitors" in many reactions involving radicals as intermediates by virtue of their ability to act as scavengers toward these radicals.

If the rate of a reaction in the absence of inhibitor is v_0 and that in the presence of a certain amount of inhibitor is v , the degree of inhibition (i) is given by

$$i = (v_0 - v)/v_0$$

See also mechanism based inhibition.

initiation

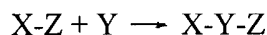
A reaction or process generating free radicals (or some other reactive reaction intermediates) which then induce a chain reaction. For example, in the chlorination of alkanes by a radical mechanism the initiation step is the dissociation of molecular chlorine.

inner-sphere (electron transfer)

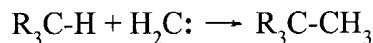
Historically an electron transfer between two metal centres sharing a ligand or atom in their respective coordination shells. The definition has more recently been extended to any situation in which the interaction between the donor and acceptor centres in the transition state is significant ($>20 \text{ kJ mol}^{-1}$). IUPAC PHOTOCHEMICAL GLOSSARY (1992). See also outer-sphere electron transfer.

insertion

A chemical reaction or transformation of the general type



in which the connecting atom or group Y replaces the bond joining the parts X and Z of the reactant XZ. An example is the carbene insertion reaction



The reverse of an insertion is called an extrusion. See also α -addition.

intermediate

A molecular entity with a lifetime appreciably longer than a molecular vibration (corresponding to a local potential energy minimum of depth greater than RT) that is formed (directly or indirectly) from the reactants and reacts further to give (either directly or indirectly) the products of a chemical reaction; also the corresponding chemical species. See reaction step, elementary reaction, stepwise reaction.



intermolecular

(1) Descriptive of any process that involves a transfer (of atoms, groups, electrons, etc.) or interactions between two or more molecular entities.

(2) Relating to a comparison between different molecular entities.

See also intramolecular.

internal return

See ion-pair return.

intimate ion pair

See ion pair.

intramolecular

(1) Descriptive of any process that involves a transfer (of atoms, groups, electrons, etc.) or interactions between different parts of the same molecular entity.

(2) Relating to a comparison between atoms or groups within the same molecular entity.

See also intermolecular.

intramolecular catalysis

The acceleration of a chemical transformation at one site of a molecular entity through the involvement of another functional ("catalytic") group in the same molecular entity, without that group appearing to have undergone change in the reaction product. The use of the term should be restricted to cases for which analogous intermolecular catalysis by chemical species bearing that catalytic group is observable. Intramolecular catalysis can be detected and expressed in quantitative form by a comparison of the reaction rate with that of a comparable model compound in which the catalytic group is absent, or by measurement of the effective molarity of the catalytic group. See also effective molarity, neighbouring group participation.

intrinsic barrier

The Gibbs energy of activation ($\Delta^\ddagger G$) in the limiting case where $\Delta G^\circ = 0$, i.e. when the effect of thermodynamic driving force is eliminated. According to the Marcus equation, the intrinsic barrier is related to the reorganization energy, λ , of the reaction by the equation

$$\Delta^\ddagger G = \lambda/4$$

CANNON (1980); SCHLESENER, AMATORE and KOCHI (1986).

inverse kinetic isotope effect

See isotope effect.

inverted micelle

The reversible formation of association colloids from surfactants in non-polar solvents leads to aggregates termed inverted (or inverse, reverse or reversed) *micelles*. Such association is often of the type



and the phenomenon of *critical micelle concentration* (or an analogous effect) is consequently not observed.

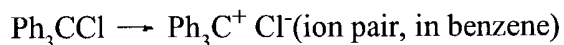
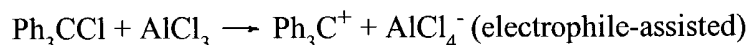
In an inverted micelle the polar *groups* of the surfactants are concentrated in the interior and the *lipophilic* groups extend towards and into the non-polar solvent.

ionic strength, I (SI unit: mol dm⁻³)

In a solution of fully dissociated electrolytes the ionic strength is defined as $I = 0.5 \sum_i c_i Z_i^2$, in which c_i is the concentration and Z_i the charge number of ionic species i . μ is also defined as $I_m = 0.5 \sum_i m_i Z_i^2$, where m_i is the molality.

ionization

The generation of one or more ions. It may occur, e.g. by loss of an electron from a neutral *molecular entity*, by the *unimolecular heterolysis* of such an entity into two or more ions, or by a heterolytic *substitution reaction* involving neutral molecules, such as



The loss of an electron from a singly, doubly, etc. charged cation is called second, third, etc. ionization. This terminology is used especially in mass spectroscopy. See also *dissociation*, *ionization energy*.

ionization energy, E_i (SI unit kJ mol⁻¹ or J per molecule)

The minimum energy required to remove an electron from an isolated *molecular entity* (in its vibrational ground state) in the gaseous phase. If the resulting molecular entity is considered to be in its vibrational ground state, one refers to the energy as the "adiabatic ionization energy". If the molecular entity produced possesses the vibrational energy determined by the Franck-Condon principle (according to which the electron ejection takes place without an accompanying change in molecular geometry), the energy is called the "vertical ionization energy". The name ionization energy is preferred to the somewhat misleading earlier name "ionization potential". See also *ionization*.

ionizing power

A term to denote the tendency of a particular solvent to promote *ionization* of an uncharged or, less often, charged solute. The term has been used both in a kinetic and in a thermodynamic context. See also

Dimroth-Reichardt E_T parameter, Grunwald-Winstein equation, Z-value.

ion pair

A pair of oppositely charged ions held together by Coulomb attraction without formation of a covalent bond. Experimentally, an ion pair behaves as one unit in determining conductivity, kinetic behaviour, osmotic properties, etc.

Following Bjerrum, oppositely charged ions with their centres closer together than a distance

$$q = 8.36 \times 10^6 Z^+ Z^- / (\epsilon_r T) \text{ pm}$$

are considered to constitute an ion pair ("Bjerrum ion pair"). [Z^+ and Z^- are the charge numbers of the ions, and ϵ_r is the relative permittivity (or dielectric constant) of the medium.]

An ion pair, the constituent ions of which are in direct contact (and not separated by an intervening solvent or other neutral molecule) is designated as a "tight ion pair" (or "intimate" or "contact ion pair"). A tight ion pair of X^+ and Y^- is symbolically represented as X^+Y^- .

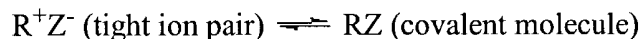
By contrast, an ion pair whose constituent ions are separated by one or several solvent or other neutral molecules is described as a "loose ion pair", symbolically represented as $X^+||Y^-$. The members of a loose ion pair can readily interchange with other free or loosely paired ions in the solution. This interchange may be detectable (e.g., by isotopic labelling) and thus afford an experimental distinction between tight and loose ion pairs.

A further conceptual distinction has sometimes been made between two types of loose ion pairs. In "solvent-shared ion pairs" the ionic constituents of the pair are separated by only a single solvent molecule, whereas in "solvent-separated ion pairs" more than one solvent molecule intervenes. However, the term "solvent-separated ion pair" must be used and interpreted with care since it has also widely been used as a less specific term for "loose" ion pair. See also common-ion effect, dissociation, ion-pair return, special salt effect.

ion pair return

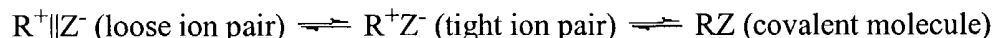
The recombination of a pair of ions R^+ and Z^- formed from ionization of RZ .

If the ions are paired as a tight ion pair and recombine without prior separation into a loose ion pair this is called "internal ion-pair return":



It is a special case of "primary geminate recombination".

If the ions are paired as a loose ion pair and form the covalent chemical species via a tight ion pair, this is called "external ion-pair return":



It is a special case of "secondary *geminate recombination*".

When the covalent molecule RZ is reformed without direct evidence of prior partial racemization or without other direct evidence of prior formation of a tight ion pair, (e.g., without partial racemization if the group R is suitably chiral) the internal ion-pair return is sometimes called a "hidden return".

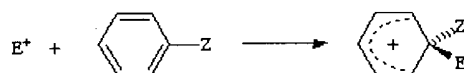
External (unimolecular) ion-pair return is to be distinguished from "external (bimolecular) ion return", the (reversible) process whereby dissociated ions are converted into loose ion pairs:



ipso-attack

The attachment of an entering group to a position in an aromatic compound already carrying a *substituent* group (other than hydrogen). The entering group may displace that substituent group but may also itself be expelled or migrate to a different position in a subsequent step. The term "ipso-substitution" is not used, since it is synonymous with substitution.

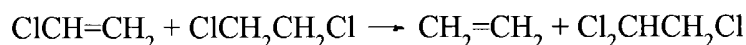
For example:



where E^+ is an *electrophile* and Z is a substituent (other than hydrogen). See also cine-substitution, tele-substitution.

isodesmic reaction

A reaction (actual or hypothetical) in which the types of bonds that are made in forming the products are the same as those which are broken in the reactants, e.g.

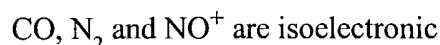


Such processes have advantages for theoretical treatment. The *Hammett equation* as applied to equilibria (cf. (a)) essentially deals with isodesmic processes.

For the use of isodesmic processes in quantum chemistry, see *HEHRE et al. (1970)*.

isoelectronic

Two or more *molecular entities* are described as isoelectronic if they have the same number of valence electrons and the same structure, i.e. number and *connectivity* of atoms, but differ in some of the elements involved. Thus



$\text{CH}_2=\text{C}=\text{O}$ and $\text{CH}_2=\text{N}=\text{N}$ are isoelectronic

CH_3COCH_3 and $\text{CH}_3\text{N}=\text{NCH}_3$ have the same number of electrons, but have different structures, hence they are not described as isoelectronic.

isoentropic

A reaction series is said to be isoentropic if the individual reactions of the series have the same standard entropy of activation.

isoequilibrium relationship

A relationship analogous to the isokinetic relationship but applied to equilibrium data. The equation defining the isoequilibrium temperature β is

$$\Delta_r H - \beta \Delta_r S = \text{constant}$$

where ΔH and ΔS are enthalpy and entropy of reaction, respectively. See also isokinetic relationship.

isokinetic relationship

When a series of structurally related substrates undergo the same general reaction or when the reaction conditions for a single substrate are changed in a systematic way, the enthalpies and entropies of activation sometimes satisfy the relation

$$\Delta^\ddagger H - \beta \Delta^\ddagger S = \text{constant}$$

where the parameter β is independent of temperature. This equation (or some equivalent form) is said to represent an "isokinetic relationship". The temperature $T = \beta$ (at which all members of a series obeying the isokinetic relationship react at the same rate) is termed the "isokinetic temperature".

Supposed isokinetic relationships as established by direct correlation of $\Delta^\ddagger H$ with $\Delta^\ddagger S$ are often spurious and the calculated value of β is meaningless, because errors in $\Delta^\ddagger H$ lead to compensating errors in $\Delta^\ddagger S$. Satisfactory methods of establishing such relationships have been devised. EXNER (1973); LEFFLER (1955). See also compensation effect, isoequilibrium relationship, isoselective relationship.

isolobal

The term is used to compare molecular fragments with each other and with familiar species from organic chemistry. Two fragments are isolobal if the number, symmetry properties, approximate energy, and shape of the frontier orbitals and the number of electrons in them are similar. See isoelectronic.

isomer

One of several species (or molecular entities) that have the same atomic composition (molecular formula) but different line formulae or different stereochemical formulae and hence different physical and/or chemical properties.

isomerization

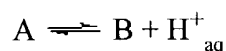
A chemical reaction, the principal product of which is isomeric with the principal reactant. An intramolecular isomerization that involves the breaking or making of bonds is a special case of a molecular rearrangement.

Isomerization does not necessarily imply molecular rearrangement (e.g. in the case of the interconversion of conformational isomers).

isosbestic point

This term is usually employed with reference to a set of absorption spectra, plotted on the same chart for a set of solutions in which the sum of the concentrations of two principal absorbing components, A and B, is constant. The curves of absorbance against wavelength (or frequency) for such a set of mixtures often all intersect at one or more points, called isosbestic points.

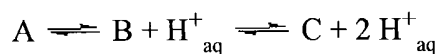
Isosbestic points are commonly met when electronic spectra are taken (a) on a solution in which a chemical reaction is in progress (in which case the two absorbing components concerned are a reactant and a product, A + B), or (b) on a solution in which the two absorbing components are in equilibrium and their relative proportions are controlled by the concentration of some other component, typically the concentration of hydrogen ions, e.g., an acid-base indicator equilibrium.



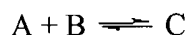
The effect may also appear (c) in the spectra of a set of solutions of two unrelated non-interacting components having the same total concentration. In all these examples, A (and/or B) may be either a single chemical species or a mixture of chemical species present in invariant proportion.

If A and B are single chemical species, isosbestic points will appear at all wavelengths at which their molar absorption coefficients (formerly called extinction coefficients) are the same. (A more involved identity applies when A and B are mixtures of constant proportion.)

If absorption spectra of the types considered above intersect not at one or more isosbestic points but over progressively changing wavelength, this is prima facie evidence in case (a) for the formation of a reaction intermediate in substantial concentration ($A \rightarrow C \rightarrow B$), in case (b) for the involvement of a third absorbing species in the equilibrium, e.g.



or in case (c) for some interaction of A and B, e.g.,



isoselective relationship

A relationship analogous to the isokinetic relationship, but applied to selectivity data of reactions. At the isoselective temperature, the selectivities of the series of reactions following the relationship are identical. GIESE (1984). See also isoequilibrium relationship, isokinetic relationship.

isotope effect

The effect on the rate or equilibrium constant of two reactions that differ only in the isotopic composition of one or more of their otherwise chemically identical components is referred to as a kinetic isotope effect (see *isotope effect, kinetic*) or a thermodynamic (or equilibrium) isotope effect (see *isotope effect, thermodynamic*), respectively.

isotope effect, equilibrium

See *isotope effect, thermodynamic*.

isotope effect, heavy atom

An *isotope effect* due to isotopes other than those of hydrogen.

isotope effect, intramolecular

A kinetic *isotope effect* observed when a single substrate, in which the isotopic atoms occupy equivalent reactive positions, reacts to produce a non-statistical distribution of *isotopologue* products. In such a case the isotope effect will favor the pathway with lower force constants for displacement of the isotopic nuclei in the *transition state*.

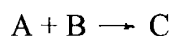
isotope effect, inverse

A kinetic *isotope effect* which $k^l/k^h < 1$, i.e. the heavier substrate reacts more rapidly than the lighter one, as opposed to the more usual "normal" isotope effect, in which $k^l/k^h > 1$. The isotope effect will normally be "normal" when the frequency differences between the isotopic *transition states* are smaller than in the reactants. Conversely, in inverse isotope effect can be taken as evidence for an increase in the corresponding force constants on passing from the reactant to the transition state.

isotope effect, kinetic

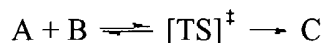
The effect of isotopic substitution on a rate constant is referred to as a kinetic isotope effect.

For example in the reaction



the effect of isotopic substitution in reactant A is expressed as the ratio of rate constants k^l/k^h , where the superscripts l and h represent reactions in which the molecules A contain the light and heavy isotopes, respectively.

Within the framework of *transition state* theory in which the reaction is rewritten as



and with neglect of isotopic mass on *tunnelling* and the transmission coefficient, k^l/k^h can be regarded as if it were the equilibrium constant for an isotope exchange reaction between the transition state $[TS]^{\ddagger}$ and the isotopically substituted reactant A, and calculated from their vibrational frequencies as in the case of a thermodynamic isotope effect (see *isotope effect, thermodynamic*).

Isotope effects like the above, involving a direct or indirect comparison of the rates of reaction of *isotopologues*, are called "intermolecular", in contrast to intramolecular isotope effects (see *isotope effect, intramolecular*), in which a single substrate reacts to produce a non-statistical distribution of isotopologue product molecules. See WOLFSBERG (1972).

isotope effect, primary

A kinetic isotope effect attributable to isotopic substitution of an atom to which a bond is made or broken in the *rate-controlling step* or in a *pre-equilibrium* step of a specified reaction is termed a primary isotope effect. The corresponding isotope effect on the equilibrium constant of a reaction in which one or more bonds to isotopic atoms are broken, is called a "primary equilibrium isotope effect". See also *isotope effect, secondary*.

isotope effect, secondary

A kinetic isotope effect that is attributable to isotopic substitution of an atom to which bonds are neither made nor broken in the *rate-controlling step* or in a *pre-equilibrium* step of a specified reaction, and is therefore not a primary isotope effect, is termed a secondary isotope effect. One speaks of α , (etc.) secondary isotope effects, where α , β (etc.) denote the position of isotopic substitution relative to the reaction centre. The corresponding isotope effect on the equilibrium constant of such a reaction is called a "secondary equilibrium isotope effect".

Secondary isotope effects have been discussed in terms of the conventional electronic effects of physical organic chemistry, e.g. induction, *hyperconjugation*, *hybridization*, etc., since these properties are determined by the electron distribution, that depends on vibrationally averaged bond lengths and angles which vary slightly with isotopic substitution. While this usage is legitimate, the term "electronic isotope effect" should be avoided, because of the misleading implication that such an effect is electronic rather than vibrational in origin. See also *isotope effect, steric*.

isotope effect, solvent

A kinetic or equilibrium isotope effect resulting from change in the isotopic composition of the solvent.

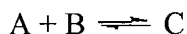
isotope effect, steric

A secondary isotope effect attributed to the different vibrational amplitudes of *isotopologues*. For example, both the mean and mean-square amplitudes of vibrations associated with C-H bonds are greater than those of C-D bonds. The greater effective bulk of molecules containing the former may be manifested by a *steric effect* on a rate or equilibrium constant.

isotope effect, thermodynamic

The effect of isotopic substitution on an equilibrium constant is referred to as a thermodynamic (or equilibrium) isotope effect.

For example, the effect of isotopic substitution in reactant A that participates in the equilibrium:



is the ratio K^l/K^h of the equilibrium constant for the reaction in which A contains the light isotope to that in

which it contains the heavy isotope. The ratio can be expressed as the equilibrium constant for the isotopic exchange reaction:



in which reactants such as B that are not isotopically substituted do not appear.

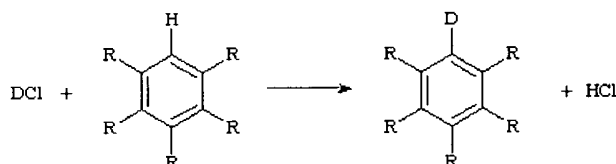
The potential energy surfaces of isotopic molecules are identical to a high degree of approximation, so thermodynamic isotope effects can only arise from the effect of isotopic mass on the nuclear motions of the reactants and products, and can be expressed quantitatively in terms of partition function ratios for nuclear motion:

$$\frac{K^l}{K^h} = \frac{(\mathcal{Q}_{\text{nuc}}^l / \mathcal{Q}_{\text{nuc}}^h)_C}{(\mathcal{Q}_{\text{nuc}}^l / \mathcal{Q}_{\text{nuc}}^h)_A}$$

Although the nuclear partition function is a product of the translational, rotational and vibrational partition functions, the isotope effect is determined almost entirely by the last named, specifically by vibrational modes involving motion of isotopically different atoms. In the case of light atoms (i.e. protium vs. deuterium or tritium) at moderate temperatures, the isotope effect is dominated by zero-point energy differences. WOLFSBERG (1972). See also *fractionation factor*.

isotope exchange

A chemical reaction in which the reactant and product chemical species are chemically identical but have different isotopic composition. In such a reaction the isotope distribution tends towards equilibrium (as expressed by fractionation factors) as a result of transfers of isotopically different atoms or groups. For example,

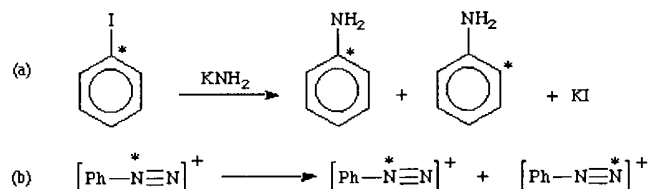


isotopic perturbation, method of

NMR shift difference measurement of the isotope effect on a fast (degenerate) equilibrium between two, except for isotopic substitution, species which are equivalent. This can be used to distinguish a rapidly equilibrating mixture with time-averaged symmetry from a single structure with higher symmetry. SIEHL (1987).

isotopic scrambling

The achievement, or the process of achieving, an equilibrium distribution of isotopes within a specified set of atoms in a chemical species or group of chemical species. For example,



(* denotes position of an isotopically different atom.)

See also *fractionation factor*.

isotopologue

A *molecular entity* that differs only in isotopic composition (number of isotopic substitutions), e.g. CH₄, CH₃D, CH₂D₂...

isotopomer

Isomers having the same number of each isotopic atom but differing in their positions. The term is a contraction of "isotopic isomer".

Isotopomers can be either constitutional isomers (e.g. CH₂DCH=O and CH₃CD=O) or isotopic stereoisomers (e.g. (*R*)- and (*S*)-CH₃CHDOH or (*Z*)- and (*E*)-CH₃CH=CHD). IUPAC STEREOCHEMICAL TERMINOLOGY (1993).

isovalent hyperconjugation

See *hyperconjugation*.

References

BERNASCONI, C. F. (1992), *Adv. Phys. Org. Chem.*, **27**, 119-238.

CANNON, R. D. (1980), "Electron Transfer Reactions", Butterworths, London.

EHRENSON, S., BROWNLEE, R. T. C., and TAFT, R. W. (1973), *Progr. Phys. Org. Chem.*, **10**, 1-80.

EXNER, O. (1973), *Progr. Phys. Org. Chem.*, **10**, 411-482.

GIESE, B. (1984), *Acc. Chem. Res.*, **17**, 438-442.

HEHRE, W. J., DITCHFIELD, R., RADOM, L., and POPL, J. A. (1970), *J. Am. Chem. Soc.*, **92**, 4796-4801.

INGOLD, C. K. (1953), "Structure and Mechanism in Organic Chemistry", Cornell University Press, New York.

*IUPAC PHOTOCHEMICAL GLOSSARY (1992). IUPAC: Organic Chemistry Division: Commission on Photochemistry. Glossary of Terms Used in Photochemistry. Draft 1, provisional.

*IUPAC STEREOCHEMICAL TERMINOLOGY (1993). IUPAC: Organic Chemistry Division: Basic Terminology of Stereochemistry. IDCNS and public review. Now published as Basic Terminology of Stereochemistry (IUPAC Recommendations 1996) in *Pure Appl. Chem.*, **68**, 2193-2222 (1996).

LEFFLER, J. E. (1955), *J. Org. Chem.*, **20**, 1202-1231.

SCHLESENER, C. J., AMATORE, C., and KOCHI, J. K. (1986), *J. Phys. Chem.*, **90**, 3747-3756.

SIEHL, H.-U. (1987), *Adv. Phys. Org. Chem.*, **23**, 63-163.

TAFT, R. W., Jr., and TOPSOM, R. D. (1987), *Progr. Phys. Org. Chem.*, **16**, 1-83.

WOLFSBERG, M. (1972), *Acc. Chem. Res.*, **5**, 225-233.

Continue with terms starting with K and L.

Return to home page for [Glossary of terms used in Physical Organic Chemistry](#).

GLOSSARY OF TERMS USED IN PHYSICAL ORGANIC CHEMISTRY (IUPAC Recommendations 1994)

M

Continued from terms starting with K and L

Contents

macroscopic diffusion control; magic acid; magnetic equivalence; magnetization transfer; Marcus equation; Markownikoff rule; mass-law effect; matrix isolation; mean lifetime; mechanism; mechanism-based inhibition; medium; Meisenheimer adduct; melting point (corrected/uncorrected); mesolytic cleavage; mesomeric effect; mesomerism; mesophase; metastable (chemical species); metathesis; + methylene; + methylidyne; micellar catalysis; micelle; Michaelis-Menten kinetics; microscopic chemical event; microscopic diffusion control (encounter control); microscopic reversibility, principle of; migration; migratory aptitude; migratory insertion; minimum structural change, principle of; mixing control; Möbius aromaticity; moiety; molecular entity; molecularity; molecular mechanics calculation; molecular metal; molecular orbital; molecular rearrangement; molecule; More O'Ferrall-Jencks diagram; multi-centre bond; + multi-centre reaction; multident; μ (mu) and μ

macroscopic diffusion control

See mixing control.

magic acid

See superacid.

magnetic equivalence

Nuclei having the same resonance frequency in nuclear magnetic resonance spectroscopy and also identical spin-spin interactions with the nuclei of a neighbouring group are magnetically equivalent. The spin-spin interaction between magnetically equivalent nuclei does not appear, and thus has no effect on the multiplicity of the respective NMR signals. Magnetically equivalent nuclei are necessarily also chemically equivalent, but the reverse is not necessarily true.

magnetization transfer

NMR method for determining kinetics of chemical exchange by perturbing the magnetization of nuclei in a particular site or sites and following the rate at which magnetic equilibrium is restored. The most common perturbations are saturation and inversion, and the corresponding techniques are often called "saturation transfer" and "selective inversion-recovery". See also saturation transfer.

Marcus equation

A general expression which correlates the Gibbs energy of activation ($\Delta^\ddagger G$) with the driving force ($\Delta_r G^\circ$) of the reaction:

$$\Delta^\ddagger G = (\lambda/4)(1 + \Delta_r G^\circ/\lambda)^2$$

where λ is the *reorganization energy* and $\Delta_r G^\circ$ is the standard free energy of the reaction corrected for the electrostatic work required to bring the reactants together. $\lambda/4$ is the *intrinsic barrier* of the reaction. Originally developed for *outer-sphere electron transfer* reactions, the Marcus equation has later been applied also to atom and group transfer reactions. MARCUS (1964); ALBERY (1980).

Markownikoff rule

"In the addition of hydrogen halides to unsymmetrically constituted [unsaturated] hydrocarbons, the halogen atom becomes attached to the carbon bearing the lesser number of hydrogen atoms." Originally formulated by Markownikoff (Markovnikov) to generalize the orientation in additions of hydrogen halides to simple alkenes, this rule has been extended to polar *addition reactions* as follows. "In the *heterolytic* addition of a polar molecule to an alkene or alkyne, the more electronegative (nucleophilic) atom (or part) of the polar molecule becomes attached to the carbon atom bearing the smaller number of hydrogen atoms."

This is an indirect statement of the common mechanistic observation, that the more electropositive (electrophilic) atom (or part) of the polar molecule becomes attached to the end of the multiple bond that would result in the more stable *carbenium ion* (whether or not a carbenium ion is actually formed as a *reaction intermediate* in the addition reaction). Addition in the opposite sense is commonly called "anti-Markovnikov addition". MARKOWNIKOFF (1870).

mass-law effect

At equilibrium, the product of the activities (or concentrations) of the reacting species is constant. Thus for the equilibrium



$$K = [C]^\gamma [D]^\delta / [A]^\alpha [B]^\beta$$

GULDBERG and WAAGE (1879). See also *common-ion effect*, *equilibrium*.

matrix isolation

A term which refers to the isolation of a reactive or unstable species by dilution in an inert matrix (argon, nitrogen, etc.), usually condensed on a window or in an optical cell at low temperature, to preserve its structure for identification by spectroscopic or other means. IUPAC ATMOSPHERIC GLOSSARY (1990).

mean lifetime

See *lifetime*.

mechanism

A detailed description of the process leading from the reactants to the products of a reaction, including a characterization as complete as possible of the composition, structure, energy and other properties of *reaction intermediates*, products, and *transition states*. An acceptable mechanism of a specified reaction (and there may be a number of such alternative mechanisms not excluded by the evidence) must be

consistent with the reaction stoichiometry, the *rate law*, and with all other available experimental data, such as the stereochemical course of the reaction. Inferences concerning the electronic motions which dynamically interconvert successive species along the *reaction path* (as represented by curved arrows, for example) are often included in the description of a mechanism.

It should be noted that for many reactions all this information is not available and the suggested mechanism is based on incomplete experimental data. It is not appropriate to use the term mechanism to describe a statement of the probable sequence in a set of stepwise reactions. That should be referred to as a reaction sequence, and not a mechanism. See also *Gibbs energy diagram*.

mechanism-based inhibition

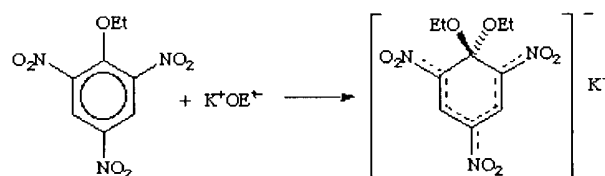
Irreversible *inhibition* of an enzyme due to its catalysis of the reaction of an artificial substrate. Also called "suicide inhibition".

medium

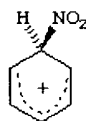
The phase (and composition of the phase) in which *chemical species* and their reactions are studied in a particular investigation.

Meisenheimer adduct

A cyclohexadienyl derivative formed as *Lewis adduct* from a *nucleophile* (*Lewis base*) and an *aromatic* or heteroaromatic compound, also called Jackson-Meisenheimer adduct. In earlier usage the term "Meisenheimer complex" was restricted to the typical Meisenheimer alkoxide *adducts* of nitro-substituted aromatic ethers, e.g.,



Analogous cationic adducts, such as



considered to be *reaction intermediates* in *electrophilic aromatic substitution reactions*, are called "Wheland intermediates", and sometimes, inappropriately, σ -complexes. JACKSON and GAZZOLO (1900); BUNCLE, CRAMPTON, STRAUSS and TERRIER. (1984). See also *σ -adduct*.

melting point (corrected/uncorrected)

The term originally signified that a correction was made (not made) for the emergent stem of the thermometer. In current usage it often means that the accuracy of the thermometer was (was not) verified. This current usage is inappropriate and should be abandoned.

mesolytic cleavage

Cleavage of a bond in a *radical ion* whereby a *radical* and an ion are formed. The term reflects the mechanistic duality of the process, which can be viewed as homolytic or heterolytic depending on how the electrons are attributed to the fragments. See MASLAK and NARVAEZ (1990).

mesomeric effect

The effect (on reaction rates, ionization equilibria, etc.) attributed to a substituent due to overlap of its p or pi orbitals with the p or pi orbitals of the rest of the *molecular entity*. *Delocalization* is thereby introduced or extended, and electronic charge may flow to or from the substituent. The effect is symbolized by M.

Strictly understood, the mesomeric effect operates in the ground electronic state of the molecule. When the molecule undergoes electronic excitation or its energy is increased on the way to the *transition state* of a *chemical reaction*, the mesomeric effect may be enhanced by the *electromeric effect*, but this term is not much used, and the mesomeric and electromeric effects tend to be subsumed in the term *resonance effect* of a *substituent*. See also *electronic effect*, *field effect*, *inductive effect*.

mesomerism

Essentially synonymous with *resonance*. The term is particularly associated with the picture of pi electrons as less localized in an actual molecule than in a *Lewis formula*.

The term is intended to imply that the correct representation of a structure is intermediate between two or more Lewis formulae. See also *aromatic* (2), *delocalization*.

mesophase

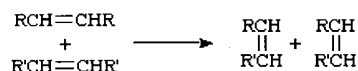
The phase of a liquid crystalline compound between the crystalline and the isotropic liquid phase.

metastable (chemical species)

See *transient (chemical species)*.

metathesis

A *bimolecular* process formally involving the exchange of a bond (or bonds) between similar interacting *chemical species* so that the bonding affiliations in the products are identical (or closely similar) to those in the reactants. For example:



(The term has its origin in inorganic chemistry with a different meaning, but this older usage is not applicable in physical organic chemistry.)

+ methylene

See *carbene*.

+ methylidyne

See *carbyne*.

micellar catalysis

The acceleration of a *chemical reaction* in solution by the addition of a surfactant at a concentration higher than its *critical micelle concentration* so that the reaction can proceed in the environment of surfactant aggregates (*micelles*). (Rate enhancements may be due, for example, to higher concentration of the reactants in that environment, more favourable orientation and solvation of the species, or enhanced rate constants in the micellar pseudophase of the surfactant aggregate.) Micelle formation can also lead to a decreased reaction rate. See also *catalyst*.

micelle

Surfactants in solution are often association colloids, that is, they tend to form aggregates of colloidal dimensions, which exist in equilibrium with the molecules or ions from which they are formed. Such aggregates are termed micelles. See also *inverted micelle*. IUPAC MANUAL APPENDIX II (1972).

Michaelis-Menten kinetics

The dependence of an initial *rate of reaction* upon the concentration of a *substrate* S that is present in large excess over the concentration of an enzyme or other *catalyst* (or reagent) E with the appearance of saturation behaviour following the Michaelis-Menten equation,

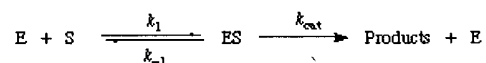
$$v = V[S]/(K_m + [S]),$$

where v is the observed initial rate, V is its limiting value at substrate saturation (i.e., $[S] \gg K_m$), and K_m the substrate concentration when $v = V/2$. The definition is experimental, i.e., it applies to any reaction that follows an equation of this general form. The symbols V_{ma} or v_{ma} are sometimes used for V .

The parameters V and K_m (the "Michaelis constant") of the equation can be evaluated from the slope and intercept of a linear plot of v^{-1} against $[S]^{-1}$ (a "Lineweaver-Burk plot") or from slope and intercept of a linear plot of v against $h/[S]$ ("Eadie-Hofstee plot").

A Michaelis-Menten equation is also applicable to the condition where E is present in large excess, in which case the concentration $[E]$ appears in the equation instead of $[S]$.

The term has sometimes been used to describe reactions that proceed according to the scheme



in which case $K_m = (k_{-1} + k_{cat})/k_1$ (Briggs-Haldane conditions). It has more usually been applied only to the special case in which $k_{-1} \gg k_{cat}$ and $K_m = k_{-1}/k_1 = K_s$; in this case K_m is a true dissociation constant (Michaelis-Menten conditions). See also *rate-determining step*.

microscopic chemical event

See *chemical reaction*, *molecularity*.

microscopic diffusion control (encounter control)

The observable consequence of the limitation that the rate of a bimolecular chemical reaction in a homogeneous medium cannot exceed the rate of encounter of the reacting molecular entities.

If (hypothetically) a bimolecular reaction in a homogeneous medium occurred instantaneously when two reactant molecular entities made an encounter, the rate of reaction would be an encounter-controlled rate, determined solely by rates of diffusion of reactants. Such a hypothetical "fully diffusion controlled rate" is also said to correspond to "total microscopic diffusion control", and represents the asymptotic limit of the rate of reaction as the rate constant for the chemical conversion of the encounter pair into product (or products) becomes large relative to the rate constant for separation (or dissociation) of the encounter pair.

"Partial microscopic diffusion control" is said to operate in a homogeneous reaction when the rates of chemical conversion and of separation are comparable. (The degree of microscopic diffusion control cannot usually be determined with any precision.) See also mixing control.

microscopic reversibility, principle of

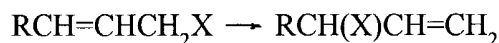
In a reversible reaction, the mechanism in one direction is exactly the reverse of the mechanism in the other direction. This does not apply to reactions that begin with a photochemical excitation. See also chemical reaction, detailed balancing.

migration

(1) The (usually intramolecular) transfer of an atom or group during the course of a molecular rearrangement.

(2) The movement of a bond to a new position, within the same molecular entity, is known as "bond migration".

Allylic rearrangements, e.g.,



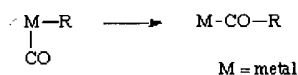
exemplify both types of migration.

migratory aptitude

The term is applied to characterize the relative tendency of a group to participate in a rearrangement. In nucleophilic rearrangements (migration to an electron-deficient centre), the migratory aptitude of a group is loosely related to its capacity to stabilize a partial positive charge, but exceptions are known, and the position of hydrogen in the series is often unpredictable.

migratory insertion

A combination of migration and insertion. The term is mainly used in organometallic chemistry.



minimum structural change, principle of

See molecular rearrangement.

mixing control

The experimental limitation of the rate of reaction in solution by the rate of mixing of solutions of the two reactants. It can occur even when the reaction rate constant is several powers of 10 less than that for an encounter-controlled rate. Analogous (and even more important) effects of the limitation of reaction rates by the speed of mixing are encountered in heterogeneous (solid/liquid, solid/gas, liquid/gas) systems. See also microscopic diffusion control, stopped flow.

Möbius aromaticity

A monocyclic array of orbitals in which there is a single out-of-phase overlap (or, more generally, an odd number of out-of-phase overlaps) reveals the opposite pattern of aromatic character to Hückel systems; with $4n$ electrons it is stabilized (aromatic), whereas with $4n + 2$ it is destabilized (antiaromatic). In the excited state $4n + 2$ Möbius pi-electron systems are stabilized, and $4n$ systems are destabilized. No examples of ground-state Möbius pi systems are known, but the concept has been applied to transition states of pericyclic reactions [see aromatic (3)].

The name is derived from the topological analogy of such an arrangement of orbitals to a Möbius strip. HEILBRONNER (1964); ZIMMERMAN (1971). See also Hückel ($4n + 2$) rule.

moiety

In physical organic chemistry moiety is generally used to signify part of a molecule, e.g. in an ester R^1COOR^2 the alcohol moiety is R^2O . The term should not be used for a small fragment of a molecule.



molecular entity

Any constitutionally or isotopically distinct atom, molecule, ion, ion pair, radical, radical ion, complex, conformer etc., identifiable as a separately distinguishable entity.

Molecular entity is used in this glossary as a general term for singular entities, irrespective of their nature, while chemical species stands for sets or ensembles of molecular entities. Note that the name of a compound may refer to the respective molecular entity or to the chemical species, e.g. methane, may mean a single molecule of CH_4 (molecular entity) or a molar amount, specified or not (chemical species), participating in a reaction.

The degree of precision necessary to describe a molecular entity depends on the context. For example "hydrogen molecule" is an adequate definition of a certain molecular entity for some purposes, whereas for others it is necessary to distinguish the electronic state and/or vibrational state and/or nuclear spin, etc. of the hydrogen molecule.

molecularity

The number of reactant molecular entities that are involved in the "microscopic chemical event" constituting an elementary reaction. (For reactions in solution this number is always taken to exclude molecular entities that form part of the medium and which are involved solely by virtue of their solvation of

solutes.) A reaction with a molecularity of one is called "unimolecular", one with a molecularity of two "bimolecular" and of three "termolecular". See also chemical reaction, order of reaction.

molecular mechanics calculation

An empirical calculational method intended to give estimates of structures and energies for conformations of molecules. The method is based on the assumption of "natural" bond lengths and angles, deviation from which leads to strain, and the existence of torsional interactions and attractive and/or repulsive van der Waals and dipolar forces between non-bonded atoms. The method is also called "(empirical) force-field calculations". BURKERT and ALLINGER (1982).

molecular metal

A non-metallic material whose properties resemble those of metals, usually following oxidative doping; e.g. polyacetylene following oxidative doping with iodine.

molecular orbital

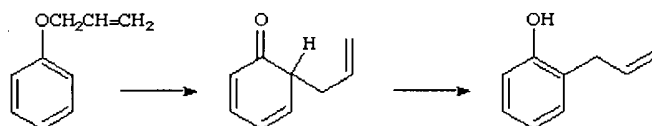
A one-electron wavefunction describing an electron moving in the effective field provided by the nuclei and all other electrons of a molecular entity of more than one atom. Such molecular orbitals can be transformed in prescribed ways into component functions to give "localized molecular orbitals". Molecular orbitals can also be described, in terms of the number of nuclei (or "centres") encompassed, as two-centre, multi-centre, etc. molecular orbitals, and are often expressed as a linear combination of atomic orbitals.

An orbital is usually depicted by sketching contours on which the wavefunction has a constant value (contour map) or by indicating schematically the envelope of the region of space in which there is an arbitrarily fixed high (say 96%) probability of finding the electron occupying the orbital, giving also the algebraic sign (+ or -) of the wavefunction in each part of that region.

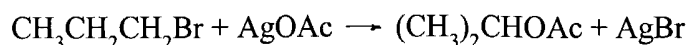
molecular rearrangement

The term is traditionally applied to any reaction that involves a change of connectivity (sometimes including hydrogen), and violates the so-called "principle of minimum structural change". According to this oversimplified principle, chemical species do not isomerize in the course of a transformation, e.g. substitution, or the change of a functional group of a chemical species into a different functional group is not expected to involve the making or breaking of more than the minimum number of bonds required to effect that transformation. For example, any new substituents are expected to enter the precise positions previously occupied by displaced groups.

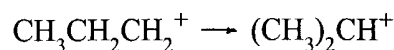
The simplest type of rearrangement is an intramolecular reaction in which the product is isomeric with the reactant (one type of "intramolecular isomerization"). An example is the first step of the Claisen rearrangement:



The definition of molecular rearrangement includes changes in which there is a migration of an atom or bond (unexpected on the basis of the principle of minimum structural change), as in the reaction



where the *rearrangement stage* can formally be represented as the "1,2-shift" of hydride between adjacent carbon atoms in the carbocation



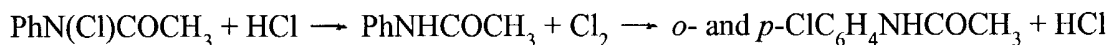
Such migrations occur also in radicals, e.g.:



The definition also includes reactions in which an *entering group* takes up a different position from the *leaving group*, with accompanying bond migration. An example of the latter type is the "allylic rearrangement":



A distinction is made between "intramolecular rearrangements" (or "true molecular rearrangements") and "*intermolecular* rearrangements" (or "apparent rearrangements"). In the former case the atoms and groups that are common to a reactant and a product never separate into independent fragments during the rearrangement stage (i.e. the change is intramolecular), whereas in an "intermolecular rearrangement" a migrating group is completely free from the parent molecule and is re-attached to a different position in a subsequent step, as in the Orton reaction:



MAYO (1980).

molecule

An electrically neutral entity consisting of more than one atom ($n > 1$). Rigorously, a molecule, in which $n > 1$ must correspond to a depression on the potential energy surface that is deep enough to confine at least one vibrational state. See also *molecular entity*.

More O'Ferrall-Jencks diagram

Visualization of the potential energy surfaces for a reacting system, as a function of two chosen coordinates. It is particularly useful to discuss structural effects on the *transition state* geometry for processes occurring either by stepwise or concerted routes. The use of such diagrams, first suggested for elimination reactions (MORE O'FERRALL (1970)), was later extended to acid-base catalysis and to certain other reactions (JENCKS (1972, 1980)).

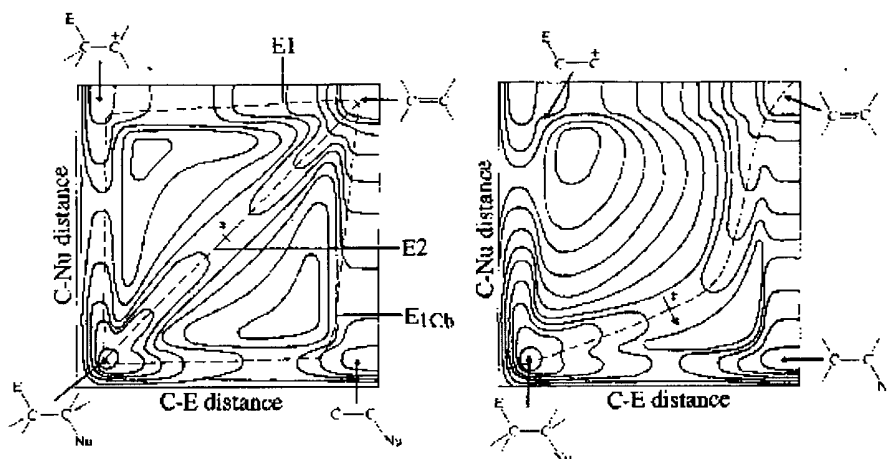


Figure. More O'Ferrall-Jencks diagrams of energy contours for β -elimination reactions as a function of lengths of the two bonds broken. Reaction coordinates follow the dotted lines. **Left:** E_2 mechanism with "central" character, simultaneous fission of C_α -Nu and C_β -H bonds. **Right:** The result of stabilization of the carbanion, $Nu-C-C^-$; a continuation of this trend would result in a switch to the $E1cb$ mechanism (Reproduced from N. S. ISAACS, "Physical Organic Chemistry", Longman Scientific, Essex, UK, (1987), with permission of Longman Scientific).

Structural changes influencing vibrational modes of the transition states cause changes in transition state geometry. Changes in the direction of the reaction coordinate (reactant or product stabilizing- or destabilizing factors) cause changes according to the *Hammond principle*. Structural changes perpendicular to the reaction coordinate (anti-Hammond effects, perpendicular effects) cause changes opposite to the Hammond behaviour, i.e., the easier the process related to the structural change, the more advanced it will be at the transition state. See WINEY and THORNTON (1975).

multi-centre bond

Representation of some *molecular entities* solely by localized two-electron two-centre *bonds* appears to be unsatisfactory. Instead, multi-centre bonds have to be considered in which electron pairs occupy orbitals encompassing three or more atomic centres. Examples include the three-centre bonds in diborane, the delocalized pi bonding of benzene, and *bridged carbocations*.

+ multi-centre reaction

A synonym for *pericyclic reaction*. The number of "centres" is the number of atoms not bonded initially, between which single bonds are breaking or new bonds are formed in the *transition state*. This number does not necessarily correspond to the ring size of the transition state for the pericyclic reaction. Thus, a Diels-Alder reaction is a "four-centre reaction". This terminology has largely been superseded by the more detailed one developed for the various pericyclic reactions. See *cycloaddition*, *sigmatropic rearrangement*.

multident

See *ambident*.

μ (μ) and μ

Notation for a ligand (prefix) that bridges two or more metal centres. The symbol μ is used for dipole

moments.

References

- ALBERY, W. J. (1980), *Annu. Rev. Phys. Chem.*, **31**, 227-263.
- BUNCEL, E., CRAMPTON, M. R., STRAUSS, M. J., and TERRIER, F. (1984), "Electron Deficient Aromatic- and Heteroaromatic- Base Interactions. The Chemistry of Anionic Sigma Complexes". Elsevier, Amsterdam.
- BURKERT, U., and ALLINGER, N. L. (1982), "Molecular Mechanics", ACS Monograph 177, American Chemical Society, Washington, D.C.
- GULDBERG, C. M., and WAAGE, P. (1879), *J. prakt. Chem.*, **19**, 69-114.
- HEILBRONNER, E. (1964), *Tetrahedron Lett.*, 1923-1928.
- ISAACS, N. S. (1987), "Physical Organic Chemistry", Longman, Essex.
- *IUPAC ATMOSPHERIC GLOSSARY (1990). IUPAC: Applied Chemistry Division: Commission on Atmospheric Chemistry. Glossary of Atmospheric Chemistry Terms, *Pure Appl. Chem.*, **62**, 2167-2219.
- *IUPAC MANUAL APPENDIX II (1972). IUPAC: Manual of symbols and terminology for physico-chemical quantities and units. Appendix II. *Pure Appl. Chem.*, **31**, 577-638.
- JACKSON, C. J., GAZZOLO, F. H. (1900), *Am. Chem. J.*, **23**, 376-396.
- JENCKS, W. P. (1972), *Chem. Rev.*, **72**, 705-718.
- JENCKS, W. P. (1980), *Acc. Chem. Res.*, **13**, 161-169.
- MARCUS, R. A. (1964), *Annu. Rev. Phys. Chem.*, **15**, 155-196.
- MARKOWNIKOFF, W. (1870), *Justus Liebigs Ann. Chem.*, **153**, 228-259 (p 256).
- MASLAK, P., and NARVAEZ, J. N. (1990), *Angew. Chem., Int. Ed. Engl.*, **29**, 283-285.
- MAYO, P. DE (1980), "Rearrangements in Ground and Excited States", Vols. I-III, Academic Press, New York.
- MORE O'FERRALL, R. A. (1970), *J. Chem. Soc. (B)*, 274-277.
- WINEY, D. A., and THORNTON, E. R. (1975), *J. Am. Chem. Soc.*, **97**, 3102-3108.
- ZIMMERMAN, H. E. (1971), *Acc. Chem. Res.*, **4**, 272-280.

Continue with terms starting with N and O.